

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
3 November 2005 (03.11.2005)

PCT

(10) International Publication Number
WO 2005/103376 A1

(51) International Patent Classification⁷: **D21H 13/26**

(21) International Application Number:
PCT/US2005/012996

(22) International Filing Date: 15 April 2005 (15.04.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10/826,530 16 April 2004 (16.04.2004) US

(71) Applicant (for all designated States except US): **E.I. DUPONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US)**

(72) Inventor; and

(75) Inventor/Applicant (for US only): **LEVIT, Mikhail, R. [US/US]; 1018 Baldwin Road, Richmond, VA 23229 (US)**

(74) Agent: **STRICKLAND, Frederick, D.; E. I. Du Pont De Nemours And Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, DE 19805 (US)**

(81) Designated States (unless otherwise indicated, for every kind of national protection available): **AE, AG, AL, AM,**

AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): **ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG)**.

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2005/103376 A1

(54) Title: ARAMID PAPER BLEND

(57) Abstract: The present invention relates to aramid paper which is suitable for composite structures and which is made using a combination of para aramid pulp, floc, and, optionally, a polymer binder material.

TITLE OF INVENTION

Aramid Paper Blend

BACKGROUND OF THE INVENTION

5 1. **Field of the Invention**

This invention relates to aramid paper suitable for composite structures.

2. **Description of Related Art**

10 History of aramid papers can be tracked from U.S. Patent No. 2,999,788, issued to Morgan on September 12, 1961, which discloses papers based on fibrils from synthetic polymers including papers from aromatic polyamide (aramid) fibrils and their combination with different fibers.

15 In the following years, many types of paper and pressboard based on aramid fibrils, aramid floc, aramid pulp, other ingredients and their combinations were described.

U.S. Patent Nos. 4,698,267 and 4,729,921, both to Tokarsky, disclose high density p-aramid papers, which comprise p-aramid floc, 20 p-aramid pulp or their blend and, optionally, 5-15% of polymeric binder including aramid fibrils.

U.K. Research Disclosure V338(073)(Anonymous), issued 1992, discloses aramid fiber containing sheets with 40-60% by weight of m-aramid fibrils, 0-30% by weight of m-aramid floc, 0-60% by weight of p-aramid floc, and 0-40% by weight of p-aramid pulp.

U.S. Patent No. 5,026,456 to Hesler et al. discloses a high porosity paper comprising 10-40% by weight of aramid fibrils, 5-30% by weight of high temperature resistant floc, and 30-85% by weight of aramid paper pulp prepared by comminuting dry aramid paper containing 50 to 60% aramid fibrils and 40 to 50% aramid floc to a particle size capable of passing through a sorting screen of 6.4-12.7 mm. More specifically, the high porosity paper of this invention comprises previously-dried aramid fibrils and previously-dried aramid floc from aramid paper pulp and, also, fresh aramid fibrils and fresh high temperature resistant floc.

PCT/US05/12996

U.S. Patent No. 5,789,059 to Nomoto discloses a honeycomb core made from a base sheet a mixture of p-aramid fibers (floc) and m-aramid pulp wherein p-aramid fiber occupies of from not less than 20% to less than 50% by weight of the mixture.

5

BRIEF SUMMARY OF THE INVENTION

This invention relates to aramid paper for composite structures, which comprises 50 to 95 weight percent p-aramid pulp, 5-50 weight percent of floc with initial modulus lower than 3000 cN/tex, and, optionally, 10 less than 20 weight percent of polymer binder material. The invention is also directed to a process for making the paper.

DETAILED DESCRIPTION OF THE INVENTION

Aramid papers find use, among others, as a basic material for 15 honeycomb cores, a reinforcement for printed circuit boards and other laminate structures, an electrical insulation in oil or resin-filled systems, as a basic material for friction facings in automotive industry, and in other applications of high performance composite structures. For higher stiffness, strength, better dimensional stability and abrasion resistance of a 20 final composite structure, such papers should preferably contain p-aramid fibrous components.

For acceptable uniformity, papers with p-aramid floc in the composition are formed from very dilute slurries (0.01-0.05 wt.%), which require a usage of special machines for wet-laid nonwovens (inclined wire 25 and others). Paper containing only p-aramid pulp as the aramid component can be formed uniformly on a regular horizontal papermaking machine, such as a Fourdrinier, from medium diluted slurries (0.2-0.6 wt.%). However, aramid paper based only on pulp does not have enough 30 strength to be produced stably at a relatively low basis weight (e.g., below 70 g/m²) and to be processed successfully into a final structure. Addition of any quantity of p-aramid floc to p-aramid pulp significantly reduces the uniformity of the sheet formed on the Fourdrinier machine and requires the aforementioned special machines for uniform formation. Also, addition of p-aramid floc to the paper composition makes the paper much stiffer,

which can require special methods to avoid problems in processing into a final composite structure, as it is described, for example, in U.S. Patent No. 6,592,963.

I have found that a combination of 50-95% by weight of p-aramid pulp, 5-50% by weight of floc having an initial modulus lower than 3000 cN/tex and optionally, less than 20% by weight of polymer binder material provides a paper composition, which can be processed stably and uniformly on a Fourdrinier type papermaking machine into a final paper. Such paper, with a basis weight below 70 g/m², can exhibit a stiffness comparable to that of m-aramid papers.

Further, after resin impregnation to form a composite paper structure, mechanical properties (strength and stiffness) can be achieved that are much higher than those achieved with an m-aramid composition. Such composite paper structure can approach the properties achieved in compositions with p-aramid floc. In fact, the composite paper structure of this invention exhibits an increase in stiffness of 4-5 times in contrast to less than 2 times for commercial meta-aramid papers or para-aramid papers based on para-aramid floc. Resins for impregnating the paper to form the composite paper structure include polyamides, polyimides, epoxies, phenolics, polyesters, polyurethanes and others equally suitable.

With an optimized composition, the paper of this invention can exhibit lower changes in dimensions with a change in temperature (i.e., a lower coefficient of thermal expansion) in comparison with commercial papers based on para- or meta-aramid papers for honeycombs.

By "floc" is meant fibers having a length of 2 to 25 millimeters, preferably 3 to 7 millimeters and a diameter of 3 to 20 micrometers, preferably 5 to 14 micrometers. If the floc length is less than 3 millimeters, its impact on the paper strength is not high enough and if it is more than 25 millimeters, it is almost impossible to form a uniform web by a wet-laid method. If the floc diameter is less than 5 micrometers, it can be difficult to produce it with enough uniformity and reproducibility and if it is more than 20 micrometers, it is virtually impossible to form uniform paper of light to medium basis weights. Floc is generally made by cutting continuous spun filaments into specific-length pieces. A preferred type of the floc in

PCT/US05/12996

this invention is meta-aramid floc and, particularly, floc from

poly(metaphenylene isophthalamide). However, floc from other materials with an initial modulus lower than 3000 cN/tex can be used, for example, poly(ethylene terephthalate), polyacrylonitrile, etc.

5 The term "pulp", as used herein, means particles of aramid material having a stalk and fibrils extending generally therefrom, wherein the stalk is generally columnar and about 10 to 50 micrometers in diameter and the fibrils are fine, hair-like members generally attached to the stalk measuring only a fraction of a micrometer or a few micrometers in diameter and about
10 10 to 100 micrometers long.

The term "fibrids" as used herein, means a very finely-divided polymer product of small, filmy, essentially two-dimensional, particles known having a length and width on the order of 100 to 1000 micrometers and a thickness only on the order of 0.1 to 1 micrometer. Fibrids are
15 made by streaming a polymer solution into a coagulating bath of liquid that is immiscible with the solvent of the solution. The stream of polymer solution is subjected to strenuous shearing forces and turbulence as the polymer is coagulated.

"Aramid" materials are polyamides wherein at least 85% of the
20 amide (-CO-NH-) linkages are attached directly to two aromatic rings. Additives can be used with the aramid and it has been found that up to as much as 10 percent, by weight, of other polymeric material can be blended with the aramid. Copolymers can be used having as much as 10 percent of other diamines substituted for the diamine of the aramid or as much as
25 10 percent of other diacid chlorides substituted for the diacid chloride of the aramid.

Floc, p-aramid pulp and a polymer binder material in the paper of this invention can be of natural color or colored by dyes or pigments. The floc and the pulp can be treated by materials which alter their surface
30 characteristics so long as such treatment does not adversely affect the ability of binders to contact and hold to the fiber surfaces.

It has been determined that to achieve higher strength in the papers of this invention that it is preferable to have a polymer binder material in the paper composition in the quantity up to 20% by weight of

PCT/US05/12996

the total composition, but at least about 3%. If more than 20% by weight of the polymer binder is present in the paper composition it can complicate the impregnation of the paper with resins in the further processing into the final composite structure and exceed necessary level of binder for 5 strengthening purposes.

Aramid fibrils are very effective types of binder. Other polymer binders such as floc, which can be fused during drying or calendering operations, or water-soluble resins, or combinations of different types of polymer binders can be used for this invention. In the case of fusible floc, 10 it performs two functions in the paper composition of this invention in that it works as floc to prevent paper breaks during paper formation and works as a binder after further processing. Depending on the type of polymer binder material and its content in the paper composition, the paper of this invention can have very high permeability, with Gurley air resistance of 15 several seconds, or have medium permeability, with Gurley air resistance up to several thousand seconds.

The preferred material for the fibrils of this invention are generally aramids, specifically, meta-aramids, and, more specifically, poly(m-phenylene isophthalamide). Other suitable fibril materials are 20 polyacrylonitrile, polycaproamide, poly (ethylene terephthalate), and the like. Fibrils from aramid materials will provide better thermal stability of the paper in comparison with other mentioned materials.

Resin used as a binder can be in the form of a water-soluble or dispersible polymer added directly to the paper making dispersion or in the 25 form of thermoplastic binder fibers of the resin material intermingled with the aramid fibers to be activated as a binder by heat applied during drying or following additional compression and/or heat treatment. The preferred materials for the water-soluble or dispersible binder polymer are water-soluble or water-dispersible thermosetting resins such as polyamide 30 resins, epoxy resins, phenolic resins, polyureas, polyurethanes, melamine formaldehyde resins, polyesters and alkyd resins, generally. Particularly useful are water-soluble polyamide resins, typical for the papermaking industry (e.g., cationic wet-strength resin KYMENE® 557LX and others).

Water solutions and dispersion of non-cured polymers can be used as well (poly(vinyl alcohol), poly(vinyl acetate), etc.).

Thermoplastic binder floc can be made from such polymers as poly(vinyl alcohol), polypropylene, polyester and the like and should have 5 a length and diameter similar to those of the floc described above.

Additional ingredients such as fillers for the adjustment of paper conductivity and other properties, pigments, antioxidants, etc in powder or fibrous form can be added to the paper composition of this invention.

The paper of this invention can be formed on equipment of any 10 scale from laboratory screens to commercial-sized papermaking machinery, such as a Fourdrinier or inclined wire machines. The general process involves making a dispersion of p-aramid pulp, floc, and a binder material (if desired) in an aqueous liquid, draining the liquid from the dispersion to yield a wet composition and drying the wet paper 15 composition. The dispersion can be made either by dispersing the fibers and then adding the binder material or by dispersing the binder material and then adding the fibers. The dispersion can also be made by combining a dispersion of fibers with a dispersion of the binder material. The concentration of fibers in the dispersion can range from 0.01 to 1.0 20 weight percent based on the total weight of the dispersion. The concentration of a binder material in the dispersion can be up to 20 weight percent based on the total weight of solids.

The aqueous liquid of the dispersion is generally water, but may include various other materials such as pH-adjusting materials, forming 25 aids, surfactants, defoamers and the like. The aqueous liquid is usually drained from the dispersion by conducting the dispersion onto a screen or other perforated support, retaining the dispersed solids and then passing the liquid to yield a wet paper composition. The wet composition, once formed on the support, is usually further dewatered by vacuum or other 30 pressure forces and further dried by evaporating the remaining liquid.

A next step, which can be performed if higher density and strength are desired, is calendering one or more layers of the paper in the nip of metal-metal, metal-composite, or composite-composite rolls. Alternatively, one or more layers of the paper can be compressed in a platen press at a

pressure, temperature and time, which are optimal for a particular composition and final application. Also, heat-treatment as an independent step before, after or instead of calendering or compression, can be conducted if strengthening or some other property modification is desired

5 without or in addition to densification.

The paper of this invention is useful as a component in structural materials such as core structures or honeycombs. For example, one or more layers of the aramid paper may be used as the primary material for forming the cells of a honeycomb structure. Alternatively, one or more

10 layers of the aramid paper may be used in the sheets for covering or facing the honeycomb cells or other core materials. Preferably, these laminates are impregnated with a resin such as a phenolic, epoxy, polyimide or other resin. However, in some instances the paper may be useful without any resin impregnation. In addition to structural

15 applications, the paper of this invention is also useful where thermal dimensional stability is desired, such as printed wiring boards; or where dielectric properties are useful, such as electrical insulating material for use in motors, transformers and other power equipment. In these applications, the paper of this invention can be used either with or without

20 impregnating resins, as desired.

TEST METHODS

Tensile Strength, Modulus, Tensile Stiffness, and Tensile Index were determined for papers and composites of this invention on an

25 Instron-type testing machine using test specimens 2.54 cm wide and a gage length of 18 cm in accordance with ASTM D 828.

Thickness and Basis Weight (Grammage) of papers and composites was determined in accordance with ASTM D 645 and ASTM D 646 correspondingly.

30 Density (Apparent Density) of papers was determined in accordance with ASTM D 202.

Specific Stiffness of Papers was determined as a mathematical quantity calculated by dividing tensile stiffness of a paper by basis weight of a paper.

Specific Stiffness of Composites was determined as a mathematical quantity calculated by dividing tensile stiffness of a composite by basis weight of a raw paper.

Specific Tensile Index for Composites was determined as a

5 mathematical quantity calculated by dividing tensile strength of a composite by basis weight of a raw paper.

10 Gurley Air Resistance for papers was determined by measuring air resistance in seconds per 100 milliliters of cylinder displacement for approximately 6.4 square centimeters circular area of a paper using a pressure differential of 1.22 kPa in accordance with TAPPI T 460.

Coefficient of Thermal Expansion in Plane was measured on dried strips of the material with dimensions of about 8.7 mm long and 2 mm wide on a 2940 TMA Instrument at a temperature between 20°C and 100°C with the temperature increasing at 10°C/minute. The loads were 2 grams and 36 grams for the paper and resin paper, respectively. The average of the readings for the machine and cross direction of the paper web was reported as the final number.

EXAMPLES

20 **Example 1**

An aqueous dispersion was made of never-dried meta-aramid fibrils at a 0.5% consistency (0.5 weight percent solid materials in water). Para-aramid pulp was dispersed in a pulper at 0.2% consistency for 5 minutes. After that the pulp dispersion was added into a tank with the 25 fibril dispersion. After ten minutes of continued agitation, meta-aramid floc was added. After five additional minutes of agitation, water was added to yield a final consistency of 0.2%. The solid materials were:

Para-aramid pulp - 74%.

Meta-aramid fibrils - 17%

30 Meta-aramid floc - 9%

The para-aramid pulp was poly (paraphenylene terephthalamide) pulp type 1F361 (sold by E.I. du Pont de Nemours and Company (DuPont), Wilmington, DE under the trade name KEVLAR®). The meta-

aramid fibrils were made from poly(metaphenylene isophthalamide) as described in U.S. Pat No. 3,756,908. The meta-aramid floc was poly(metaphenylene isophthalamide) floc of linear density 0.22 tex (2.0 denier) and length of 0.64 cm with an initial modulus of about 800 cN/tex

5 (sold by DuPont under the trade name NOMEX®). The resulting dispersion was pumped to a supply chest and fed from there to a Fourdrinier machine to make paper with a basis weight of 47.5 g/m². Other properties of the paper are described in the Table 1 below.

10 **Example 2**

A slurry was prepared as in Example 1. A paper with a basis weight of 40.7 g/m² was formed on a Fourdrinier. Other properties of the paper are described in the Table 1 below.

15 **Comparative Example 3**

A slurry was prepared as in Example 1, but without addition of the floc in the composition. The solid materials were:

Para-aramid pulp - 80%.

Meta-aramid fibrils - 20%

20 The resulting dispersion was pumped to a supply chest and fed from there to a Fourdrinier to make paper with a basis weight of 47.5 and 60 g/m². However, frequent breaks occurred and it was impossible to prepare a continuous sheet.

25 **Comparative Example 4**

Para-aramid pulp as used in Ex. 1 was dispersed in the pulper at 0.2% consistency for 5 minutes. The resulting dispersion was pumped to a supply chest and fed from there to a Fourdrinier to make paper with a basis weight of 50 and 60 g/m². However, frequent breaks occurred and it

30 was impossible to prepare a continuous sheet.

Example 5

The paper from Example 1 was passed through the nip of a metal-metal calender with a roll diameter of about 20 cm at a temperature of

about 300°C and a linear pressure of about 1200 N/cm. Properties of the final paper are shown in Table 1.

Example 6

5 The paper from Example 2 was passed through the nip of a metal-metal calender with a roll diameter of about 20 cm at a temperature of about 300°C and linear pressure of about 1200 N/cm.

Properties of the final paper are shown in Table 1.

10 **Example 7**

The paper from Example 1 was compressed for 2 minutes in a platen press at a temperature of about 304°C and a pressure of about 3.45 MPa.

Properties of the final paper are shown in Table 1.

15

Example 8

The paper from Example 1 was compressed for 5 minutes in the platen press at a temperature of about 327°C and a pressure of about 10.8 MPa.

20

Properties of the final paper are shown in Table 1.

Example 9

1.5 g (based on dry weight) of para-aramid pulp was placed in a Waring Blender with 800 ml of water and agitated for 3 min. After that, 25 34.5 g of an aqueous, never-dried, meta-aramid fibrid slurry (0.58% consistency and freeness 330 ml of Shopper-Riegler), the prepared water dispersion of the para-aramid pulp from the Waring Blender and 0.3 g of meta-aramid floc were placed together in a laboratory mixer (British pulp evaluation apparatus) with about 1600 g of water and agitated for 1 min.

30

The solid materials in the slurry were:

Para-aramid pulp - 75%

Meta-aramid floc - 15%

Meta-aramid fibrils - 10%

PCT/US05/12996

The para-aramid pulp, the meta-aramid floc and meta-aramid fibrils were the same as described in Example 1. The dispersion was poured, with 8 liters of water, into an approximately 21 x 21 cm handsheet mold and a wet-laid sheet was formed. The sheet was placed between 5 two pieces of blotting paper, hand couched with a rolling pin and dried in a handsheet dryer at 190°C.

After drying, the sheet was passed through the nip of a metal-metal calender with a roll diameter of about 20 cm at a temperature of about 270°C and a linear pressure of about 3000 N/cm.

10 The final paper had a basis weight of 56.6 g/m².

Other properties of the paper are described in the Table 1 below.

Examples 10-13

15 The papers were prepared as described in Example 9, but with varying percentages of the three components (para-aramid pulp, meta-aramid floc, and meta-aramid fibrils).

The percentages of the components of the paper compositions and their properties are shown in Table 1.

20 **Example 14**

1.2 g (based on dry weight) of para-aramid pulp was placed in a Waring Blender with 800 ml of water and was agitated for 3 min. After that, the prepared water dispersion of the para-aramid pulp, 0.3 g of poly (vinyl alcohol) floc and 0.5 g of meta-aramid floc were placed together in a 25 laboratory mixer (British pulp evaluation apparatus) with about 1600 g of water and agitated for 1 min.

The solid materials in the slurry were:

Para-aramid pulp - 60%

Meta-aramid floc - 25%

30 Poly (vinyl alcohol) floc - 15%

The para-aramid pulp and the meta-aramid floc were the same as described in Example 1. Poly (vinyl alcohol) floc was type VPB105-1 with linear density 0.11 tex and cut length 3 mm (sold by KURARAY Co. under trade name Kuralon VP). Its initial modulus was lower than 530 cN/tex as

The dispersion was poured, with 8 liters of water, into an approximately 21 x 21 cm handsheet mold and a wet-laid sheet was 5 formed. The sheet was placed between two pieces of blotting paper, hand couched with a rolling pin and dried in a handsheet dryer at 190°C. After drying, the sheet was compressed for 5 min. in a platen press at a temperature about 304°C and a pressure about 10.8 MPa.

Properties of the final paper are described in Table 1.

10

Examples 15-16

The papers were prepared as in Example 14, but with varying percentages of the three components (para-aramid pulp, meta-aramid floc and poly (vinyl alcohol) floc).

15 The percentages of the components of the paper compositions and their properties are shown in Table 1.

Example 17

The paper was prepared as in Example 14, except that a water-soluble resin was added to the paper composition in the quantity of 5 20 percent by weight based on the total weight of the composition. The water-soluble resin was KYMENE 557LX sold by Hercules. Paper compositions and properties are shown in Table 1.

Example 18

The paper was prepared as in Example 15, except that the water-soluble resin was added to the paper composition in the quantity of 5 25 percent by weight based on the total weight of the composition. The resin was the same as in Example 23. Paper compositions and properties are 30 shown in Table 1.

Example 19

A composite was prepared by impregnation of the paper from Example 5 with a solvent-based phenolic resin (PLYOPHEN 23900 from

PCT/US05/12996

the Durez Corporation) following by removing any excess resin from the surface with blotting paper and curing in an oven by ramping up the temperature as follows: heating from room temperature to 82°C and holding at this temperature for 15 minutes, increasing the temperature to 5 121°C and holding at this temperature for another 15 minutes and increasing the temperature to 182°C and holding at this temperature for 60 minutes. Properties of the composite are shown in Table 2.

Example 20

10 A composite was prepared as described in Example 19, except that the paper from Example 6 was used. Properties of the composite are shown in Table 2.

Comparative Example 21

15 A composite was prepared as described in Example 19 except that a para-aramid paper based on KEVLAR® floc and NOMEX® fibrils, sold by DuPont as KEVLAR® 1.8N636 paper, was used. Properties of the composite are shown in Table 2.

Comparative Example 22

20 A composite was prepared as described in Example 19 with a difference that a para-aramid paper based on KEVLAR® floc and NOMEX® fibrils, sold by DuPont as KEVLAR® 2.8N636 paper, was used. Properties of the composite are shown in Table 2.

25

Comparative Example 23

A composite was prepared as described in Example 19 with a difference that a meta-aramid paper based on NOMEX® floc and NOMEX® fibrils, sold DuPont as NOMEX® 2T412 paper, was used.

30 Properties of the composite are shown in Table 2.

PCT/US05/12996
Comparative Example 24

A composite was prepared as described in Example 19 except that a meta-aramid paper based on NOMEX® floc and NOMEX® fibrils, sold by DuPont as NOMEX® 3T412 paper was used. Properties of the 5 composite are shown in Table 2.

PCT/US2005/012996

Table 1 Properties of Papers

Example	Paper composition (wt. %)				Basis wt. (g/m ²)	Thickness (mm)	Density (g/cm ³)	Tensile strength (N/cm)	Modulus (MPa)	Gurley air resistance (seconds)
	P-Aramid Soluble Pulp	M-Aramid Fibrils Floc	PVA Fiber	Water- Resin						
1	74	9	17	49.8	0.136	0.37	3.76	241	141	10
2	74	9	17	40.0	0.113	0.35	2.84	224	91	99
Comp 3	80		20							
Comp 4	74									
5	74	9	17	49.2	0.061	0.80	8.50	1496	2700	6
6	74	9	17	40.0	0.046	0.86	7.80	1827	1170	
7	74	9	17	45.4	0.102	0.45	5.25	223	86	
8	74	9	17	49.5	0.077	0.65	6.24	1112	600	
9	75	15	10	51.2	0.048	1.06	9.04	2751	>300	
10	90	10	0	51.2	0.043	1.19	6.65	2455	32.4	
11	60	30	10	51.2	0.053	0.97	8.96	2013	112	
12	90	5	5	51.2	0.046	1.12	7.12	2972	>300	
13	75	25	0	51.5	0.051	1.01	6.40	1751	11.8	
14	60	25	15	44.7	0.076	0.59	16.90	1813	3.1	
15	85	0	15	43.7	0.116	0.38	7.74	483	2.0	
16	60	35	5	44.7	0.083	0.54	7.84	965	2.0	
17	57	23.8	14.2	5	44.4	0.121	0.37	15.0	618	0.9
18	80.8	0	14.2	5	44.7	0.121	0.37	9.47	362	1.7

Table 2 Relative Properties of Papers and Composites

Example	Paper type	Specific stiffness of paper ((N/cm)/(g/m ²))	Resin Pick-up (%) from paper	Specific stiffness of composite ((N/cm)/(g/m ²))	Specific tensile index of composite ((N/cm)/(g/m ²))	Ratio between specific stiffness of composite and paper	Coefficient of thermal expansion in plane for paper (ppm/C)	Coefficient of thermal expansion in plane for composite (ppm/C)
19	Example 5	18.5	81.8	96.9	1.42	5.2	-1	4
20	Example 6	21.0	100	95.8	1.37	4.6	-1	4
Comp21	1.8N636	77.6	83.5	103.2	1.33	1.3	-4	-2
Comp22	2.8N636	69.0	52.7	110.9	2.00	1.6	-4	-2
Comp23	2T412	29.5	44.9	42.7	0.90	1.4	24	25
Comp24	3T412	30.3	42.9	42.8	0.86	1.4	24	25

As can be seen from Table 2, the stiffness of the inventive paper is less than the stiffness of commercial paper based on p-aramid floc (i.e., comparative examples 21 and 22) and also less than even the papers 5 based on m-aramid (i.e., comparative examples 23 and 24).

However, the composites based on the inventive papers are very stiff, which is desirable for the majority of composite applications. Their stiffness is very close to that of the composites based on the p-aramid papers and much stiffer than that of the composites based on m-aramid 10 paper. This is additionally demonstrated by the ratio between specific stiffness of the composite and the respective papers on which they were based. The ratio is much higher for the inventive paper vs. the comparative papers, demonstrating that "softer" (i.e., less stiff) paper provides for easier conversion into the final composite structure.

15 Further, the paper of the invention and corresponding composites have very good dimensional stability. At the indicated temperature change, the inventive paper by itself has dimensional stability that is better than commercial papers based on p-aramid floc and much better than commercial m-aramid papers. The dimensional stability of the final 20 composite structure based on the invented paper is very close to those based on papers with p-aramid floc and much better in comparison with dimensional stability of the composites based on aramid papers.

CLAIM(S)

What is claimed is:

1. Aramid paper comprising 50 to 95 weight percent p-aramid pulp and 5-50 weight percent of floc with an initial modulus less than 3000 cN/tex.
2. The aramid paper of claim 1, wherein p-aramid pulp is poly (p-phenylene terephthalamide) pulp.
3. The aramid paper of claim 1, wherein the floc is meta-aramid.
4. The aramid paper of claim 3, wherein the meta-aramid floc is poly (m-phenylene isophthalamide) floc.
5. The aramid paper of claim 1, comprising a polymer binder material in the quantity of less than 20 weight percent based on the weight of the total composition.
6. The aramid paper of claim 5, wherein at least a portion of the polymer binder material is in the form of fibrils.
7. The aramid paper of claim 6, wherein the fibrils are made from poly (m-phenylene isophthalamide).
8. The aramid paper of claim 5, wherein the polymer binder can be fused by one of the group consisting of drying and calendering.
9. The aramid paper of claim 5, wherein at least a portion of the polymer binder material is a resin binder material, which can be fused during drying or calendering of the paper.

PCT/US05/12996

10. The aramid paper of claim 9, wherein at least a portion of the resin binder material is thermoplastic floc.

11. The aramid paper of claim 9, wherein at least a portion of the 5 resin binder material is a water-soluble resin.

12. The aramid paper of claim 1, wherein the basis weight of the paper is less than 70 g/m².

10 13. The aramid paper of claim 1 or 5, wherein the absolute value of the coefficient of thermal expansion of the paper in plane in the temperature interval between 20 and 100°C is less than 4 ppm/C.

14. The aramid paper of claim 1 or 5, comprising 70 to 95 weight 15 percent p-aramid pulp.

15. A printed wiring board, comprising one or more layers of the paper of claim 1 or 5.

20 16. An electrical insulating material, comprising one or more layers of the paper of claim 1 or 5.

17. A composite structure, comprising the aramid paper of claim 1 or 5 impregnated with a resin.

25 18. The composite structure of claim 17, wherein the resin is a phenol.

19. A printed wiring board or electrical insulating material, 30 comprising the composite structure of claim 17.

20. A structural material, comprising the aramid paper of claim 1 or 5.

21. The structural material of claim 20, wherein the aramid paper is incorporated into the cells of a honeycomb structure.

22. The structural material of claim 20, wherein the aramid paper
5 is incorporated into the facing of a sandwich panel.

23. A process of making aramid paper, comprising the steps of
dispersing p-aramid pulp in water
blending the pulp/water slurry with a floc having an initial
10 modulus less than 3000 cN/tex wherein the weight percent of the pulp and
the floc in the solids is from 50 to 95 and from 5 to 50 respectively,
draining the water from the final slurry to yield a wet paper
composition,
drying the wet paper composition.

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24. The process of claim 23, comprising a step of wet pressing
of the wet paper composition before drying.

25. The process of claim 24, comprising heat-treating the paper
20 after drying.

26. The process of claim 23, comprising a step of adding a
polymer binder material in a quantity less than 20 weight percent of the
total solids after blending the pulp/water slurry with the floc.

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27. The process of claim 26, comprising heat-treating the paper
after drying.

28. The process of claim 23, comprising densification of the
30 dried paper.

29. The process of claim 28, wherein densification is performed
by selecting one of the group consisting of application of pressure in the
nip of a calender and application of pressure in a press.

30. The process of claim 28, comprising a step of heat-treating the paper after densification.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/012996

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 D21H13/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1 152 084 A (SHOWA AIRCRAFT INDUSTRY CO., LTD) 7 November 2001 (2001-11-07) column 4, lines 5-50	1,23
X	US 4 729 921 A (TOKARSKY ET AL) 8 March 1988 (1988-03-08) column 1, line 50 - column 2, line 25	1,23
A	US 5 026 456 A (HESLER ET AL) 25 June 1991 (1991-06-25) column 1, line 35 - column 2, line 60; example 1	1-30
A	US 5 833 807 A (RAMACHANDRAN ET AL) 10 November 1998 (1998-11-10) column 2, line 57 - column 3, line 47; example 2	1-30
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
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- "O" document referring to an oral disclosure, use, exhibition or other means
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- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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- "&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 September 2005	21/09/2005
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Lanniel, G

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US2005/012996

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 739 707 A (SHOWA AIRCRAFT INDUSTRY CO., LTD) 30 October 1996 (1996-10-30) column 4, lines 27-58; claim 1	1-30
A	WO 95/17549 A (E.I. DU PONT DE NEMOURS AND COMPANY) 29 June 1995 (1995-06-29) page 1, lines 19-30; claim 1	1-30

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2005/012996

Patent document cited in search report	Publication date		Patent family member(s)	Publication date
EP 1152084	A 07-11-2001	JP	3321141 B2	03-09-2002
		JP	2001277387 A	09-10-2001
		US	6544622 B1	08-04-2003
US 4729921	A 08-03-1988	AU	584645 B2	01-06-1989
		AU	4879885 A	24-04-1986
		BR	8505185 A	29-07-1986
		CA	1261109 A1	26-09-1989
		DE	3566917 D1	26-01-1989
		DK	478385 A	20-04-1986
		EP	0178943 A1	23-04-1986
		ES	8700870 A1	01-02-1987
		GR	852531 A1	19-02-1986
		HK	35489 A	05-05-1989
		IE	57021 B1	11-03-1992
		JP	5065640 B	20-09-1993
		KR	9303396 B1	26-04-1993
		PT	81339 A	01-11-1985
		SG	10789 G	07-07-1989
US 5026456	A 25-06-1991	JP	3012365 B2	21-02-2000
		JP	4228696 A	18-08-1992
		SU	1838020 A3	30-08-1993
US 5833807	A 10-11-1998	CA	2282256 A1	22-10-1998
		CN	1252113 A	03-05-2000
		DE	69809211 D1	12-12-2002
		DE	69809211 T2	21-08-2003
		EA	1227 B1	25-12-2000
		EP	0975835 A1	02-02-2000
		ES	2183349 T3	16-03-2003
		JP	2001520711 T	30-10-2001
		UA	61947 C2	15-08-2000
		WO	9846827 A1	22-10-1998
EP 0739707	A 30-10-1996	US	5789059 A	04-08-1998
WO 9517549	A 29-06-1995	DE	69408170 D1	26-02-1998
		DE	69408170 T2	20-08-1998
		EP	0736120 A1	09-10-1996
		ES	2111394 T3	01-03-1998
		JP	9506938 T	08-07-1997
		JP	3673277 B2	20-07-2005
		RU	2125131 C1	20-01-1999